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(71) Applicant: Colgate-Palmolive Company
300 Park Avenue
New York, N.Y. 10022-7499(US)

(72) Inventor: Cush, James Frank, Jr.
386 Jackson Avenue
Washington Township, New Jersey(US)
Inventor: Kolodziej, Richard M.
72-B Cedar Lane
Highland Park, New Jersey(US)

(74) Representative: Smulders, Theodorus A.H.J., Ir. et al
Vereenigde Octrooibureaux Nieuwe Parklaan 97
NL-2587 BN 's-Gravenhage(NL)

(54) **Zeolite based spray-dried detergent compositions and process for preparing same.**

(57) A process for producing a free-flowing, zeolite-containing spray-dried particulate detergent composition is described, said detergent composition having improved particle mechanical strength and integrity concomitant with high solubility characteristics such that the amount of visible residue deposited on fabrics laundered with such detergent composition is significantly minimized comprising the steps of:

(a) forming an aqueous crutcher slurry containing (i) at least about 5%, by weight, of a zeolite; (ii) an effective amount of a defined bead strengthening agent; and (iii) from about 0 to 50%, by weight, of a supplementary detergent builder; said crutcher slurry being essentially free of sodium silicate and bentonite and containing less than about 3%, by weight, of anionic and/or nonionic surface active detergent compounds, all percentages being based on the solids content of the slurry, in the absence of water;

(b) spray-drying the crutcher slurry of step (a) to produce spray-dried particles; and

(c) applying one or more anionic, nonionic and/or cationic surface active detergent compounds to the spray-dried particles.

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The present invention relates to a process for manufacturing a free-flowing spray-dried particulate detergent composition containing a zeolite builder and at least one surface active detergent compound, which composition is characterized by improved particle strength and integrity concomitant with reduced residue deposition properties. More particularly, this invention relates to a process for producing a spray-dried detergent composition characterized by the absence of sodium silicate in the aqueous crutcher slurry and the presence of a bead strengthening agent to provide particles having desired properties of enhanced mechanical strength. The invention also relates to particulate detergent compositions produced by the aforementioned process of manufacture which have improved washing properties by virtue of providing little, if any, residue on washed fabrics as well as having excellent mechanical strength and resistance to breakage so as to allow such compositions to be extensively stored, handled and transported without causing undo abrasion or fragmentation of the particles.

Commercial detergent compositions containing water softening aluminum silicate builders, such as zeolites, have long been marketed in the United States and Europe. Recently, zeolites in commercial laundry detergent compositions have become especially prevalent due, primarily, to increased governmental concern with phosphates in sewage effluents. This concern has been manifested by legislation aimed at curbing the use of phosphates in detergent compositions because of their attributed nutritive effect in enhancing algae growth in inland waters, presumably at the expense of other forms of aquatic life. Consequently, recent years have been marked by an increased emphasis on providing low phosphate or phosphate-free commercial detergent compositions, commonly referred to as low P or zero P (or No-P) detergent products.

Zeolites, natural as well as synthetic, are known to be effective calcium sequestrants and are commonly used to replace phosphates, such as sodium tripolyphosphate, as detergent builders in commercial low-P or zero-P detergent compositions. But the presence of zeolite has heretofore often created a problem with regard to water-insoluble residue being deposited on laundry washed with such zeolite-containing compositions. This is generally attributed to its interaction with sodium silicate, a common ingredient in spray-dried particulate compositions, to form an insoluble zeolite-silicate agglomerate which becomes entrapped in the washed fabrics and forms an unsightly "residue" on the laundered clothing, seriously detracting from the washing performance.

Sodium silicate is generally considered a critical ingredient in particulate detergent compositions. It is reported to serve many functions: first, as a corrosion inhibitor to provide protection for metal parts of the washing machine which come into contact with aqueous solutions of the washing composition; second, to increase the alkalinity of the aqueous washing solution; and most important, particularly in a spray-dried composition, it serves to provide stability and integrity to the detergent particles or beads formed during the spray-drying operation.

It has now been discovered that the problem of residue deposition can be substantially avoided while maintaining bead stability and integrity in a spray-dried composition by eliminating sodium silicate from the detergent composition, substantially reducing the presence of surfactants in the crutcher slurry and incorporating into the crutcher slurry a bead strengthening agent as hereinafter described, such as sodium citrate.

Spray-dried detergent compositions containing a zeolite builder and sodium citrate are well known in the detergent art. U.S. Patent 3,801,511 to Lemoff discloses a spray-dried detergent composition in which an anti-caking agent such as sodium citrate is added to the aqueous slurry prior to spray-drying so as to provide crisp, free-flowing granules of said detergent composition. Sodium silicate is a preferred component of the detergent composition.

U.S. 4,303,556 to Llenado describes a spray-dried detergent composition containing an aluminosilicate ion exchange material, sodium silicate and optionally an auxiliary builder which may be citric acid. Anionic surfactants are added to the aqueous slurry which is spray dried. U.S. 4,861,503 to Hollingsworth discloses a low-phosphate spray-dried detergent composition prepared from a crutcher slurry containing one or more anionic or nonionic detergent active compounds; from 0 to 10% of sodium silicate; a non-phosphate builder; from 0.5 to 2.5% of a salt of succinic acid; and 0.5 to 10% of a polymeric polycarboxylate. The compositions described in the Examples contain 4 or 5% sodium silicate.

U.S. Patent 5,024,778 to Grecsek describes zeolite-containing spray dried base beads for detergent compositions which contain 5 to 60% of zeolite, 0 to 5% of water soluble silicate, 2 to 40% of bentonite and about 5 to 60% of polyphosphate. The presence of bentonite is intended to prevent the interaction of zeolite and silicate to form an objectionable aggregate which deposits on washed fabrics. The patent also discloses using citric acid and magnesium sulfate as anti-gelling processing aids to be added to the crutcher mix when the crutcher includes silicate in combination with carbonate and/or bicarbonate because of the tendency of such combination to solidify or cause gelation in the crutcher.

U.S. Patent 4,231,887 to Denney discloses zeolite agglomerates for detergent compositions in a matrix of sodium citrate and ethoxylated linear alcohol. The sodium citrate is referred to as a "crisping agent" which imparts crispness to the agglomerates while permitting them to disintegrate upon contact with water. In EP 1853 naming Smith and Maxwell as inventors there is disclosed a zeolite-containing detergent composition which also contains sodium citrate. The working Examples 1-6 at page 26 of the publication describe spray dried compositions containing a minimum of 10%, by weight, of anionic and/or nonionic detergent compounds. In some of these compositions sodium citrate and zeolite are present in the finished composition in the absence of sodium silicate. The surfactant detergent compounds are all added to the crutcher slurry; none being post-added or applied subsequent to spray drying to the spray-dried particles.

U.S. Patent 4,988,454 to Eertink et al describes a process for preparing a low or zero-phosphorous detergent powder containing zeolite, sodium silicate, surfactant and polyacrylate. The process of manufacture restricts the amount of silicate in the crutcher slurry to no more than 2%, by weight, of the silicate in the final powder, and compensates for such restricted amount of silicate by post-dosing sodium silicate with the spray-dried powder as well as incorporating a polymer or copolymer of acrylic acid as a "structuring agent".

SUMMARY OF THE INVENTION

The present invention provides a process for producing a free-flowing spray-dried particulate detergent composition having a density of from about 0.3 to about 1.0 g/cc and containing a zeolite and one or more anionic, nonionic and/or cationic surface active detergent compounds, said detergent composition having improved particle mechanical strength and integrity to allow extensive storage and handling of the composition with only minimum breakage and abrasion of the particles concomitant with high solubility characteristics such that the amount of visible residue deposited on fabrics laundered with such detergent composition is significantly minimized comprising the steps of:

(a) forming an aqueous crutcher slurry containing (i) at least about 5%, by weight, of a zeolite; (ii) an effective amount of a bead strengthening agent selected from the group consisting of citric acid, water-soluble salts of citric acid, nitrilotriacetate, water-soluble salts of nitrilotriacetate and mixtures thereof; and (iii) from about 0 to 50%, by weight, of a supplementary detergent builder other than (i) and (ii); said crutcher slurry being essentially free of sodium silicate and bentonite and containing less than about 3%, by weight, of anionic and/or nonionic surface active detergent compounds, all percentages being based on the solids content of the slurry, in the absence of water;

(b) spray-drying the crutcher slurry of step (a) to produce spray-dried particles; and

(c) applying one or more anionic, nonionic and/or cationic surface active detergent compounds to the spray-dried particles in an amount sufficient to obtain the desired detergency or softening properties for said particulate detergent composition.

The present invention further provides a spray-dried particulate detergent composition containing (a) at least 5%, by weight, of a zeolite; (b) an effective amount of a bead strengthening agent as herein defined; (c) from about 0 to 50%, by weight, of a supplementary detergent builder other than (a) and (b); and (d) one or more anionic nonionic or cationic surfactant active detergent compounds in an amount sufficient to obtain the desired properties of detergency or softening for the particulate detergent composition, said detergent composition by prepared by the process of the invention defined herein.

The detergent powders of the invention preferably have a phosphorous content of less than about 2.5%, by weight, preferably below about 1%, by weight, and most preferably are zero-P compositions.

The present invention is predicated on the discovery that, in contradistinction to the practice of the prior art, the exclusion of sodium silicate from the aqueous crutcher slurry in preparing zeolite-containing spray-dried particles, the inclusion of a bead strengthening agent as herein described and the restriction on the amount of surfactant in the crutcher slurry are three important process parameters which when practiced in combination provide a particulate detergent composition having excellent mechanical strength and integrity as well as superior washing characteristics such that fabrics laundered therewith are substantially free of the characteristic residue observed on fabrics laundered with most commercially available zeolite-containing spray-dried laundry compositions. Further, unlike the disclosure of U.S. Patent 5,024,778, the avoidance of residue is effected in the absence of bentonite.

The restriction on surfactant compounds in the crutcher slurry is required because the presence of anionic or nonionic surface active detergent compounds in the crutcher in significant amounts adversely affects the mechanical strength and integrity of the spray-dried particles leaving the tower (commonly referred to as "tower particles") as well as diminishing the absorptivity of such particles for oversprayed surfactant in a subsequent processing step. In the absence of sodium silicate, which ordinarily serves to

enhance particle integrity, anionic and nonionic surfactants have the effect of expanding the particles formed during spray-drying such that depending on the amount present, fragmented and dusty particles are formed substantially lacking mechanical strength. The addition of surfactants to the crutcher also tends to undermine the desirable free-flowing characteristics of the tower particles, producing instead a tacky particulate material having the tendency to form "clumps" or agglomerates when compressed during storage or handling. In accordance with the invention, the level of anionic and nonionic surface active compounds in the crutcher slurry is maintained below about 3%, by weight, preferably below about 1%, by weight, and most preferably is substantially free of anionic and nonionic surfactant compounds, the above percentages being based on the solids content of the slurry, in the absence of water.

Another significant feature of the process of the invention is that it is capable of providing spray-dried particulate compositions over a range of densities up to about 1.0 g/cc. This is particularly important for the manufacture of so-called concentrated and superconcentrated laundry detergent powders which require high density products capable of providing effective laundering at recommended dosages of "1/4 cup" or "1/2 cup" corresponding to about 35-45 grams or about 60-70 grams of product per wash, respectively, under U.S. washing conditions.

Conventional spray-drying processes are generally unable to manufacture spray-dried detergent compositions at densities typically required to provide an effective "1/4 cup" dosage product. In accordance with the present invention, the density of the particles leaving the spray tower can be as high as 0.8 g/cc. Further increases in density are effected during the post-addition of the surfactant detergent compounds as well as upon addition of optional post-added ingredients such as bleaches, activators, supplementary builders, clay, perfume and the like.

The density of tower particles are conveniently regulated in accordance with the invention by the addition to the crutcher slurry of an organic "density modifying agent" which lowers the density of the spray-dried particle by creating, in effect, an expanded particle or bead during spray drying. The amount of such modifying agent added to the crutcher slurry will generally be from about .01% to 5% depending on the desired density of the tower particles. Preferred density modifying agents for use herein include organic materials such as sodium toluene sulfonate and homopolymers and copolymers of acrylic acid such as with maleic anhydride or methacrylate in a range of molecular weight from 2000 to 200,000, sodium polyacrylate being particularly preferred for this purpose in a molecular weight range of 40,000 to 60,000. Other useful density modifying agents include sodium xylene sulfonate.

The bead strengthening agent is generally added to the slurry in an amount of from about 1 to about 50%, preferably at least about 3%, such as, from about 3 to 30%, and most preferably from about 5 to 20%, by weight, based on the solids content of the slurry in the absence of water. An alkali or alkaline earth metal salt of citric acid is preferred for this purpose, most preferably sodium citrate or magnesium citrate.

DETAILED DESCRIPTION OF THE INVENTION

The production of particulate detergent compositions by spray-drying is well known in the detergent industry. Generally, an aqueous crutcher slurry is formed containing a mixture of water with many or most of the ingredients desired in the final detergent composition. The solids content of the slurry is generally from about 40% to about 70%, preferably 50% to 65% thereof the balance being water. The crutcher slurry is then atomized by pumping it through a nozzle at a pressure of about 500 psi into a spray-drying tower, the typical dimensions of a commercial tower being about 35-100 feet in height and about 12-30 feet in diameter. At the base of the tower, air is introduced at a temperature of from about 300-1000°F which contacts the atomized slurry to provide a hot drying gas for the droplets of the slurry thereby evaporating most of the water. The resulting particles or beads are collected at the bottom of the tower, the moisture and heated air existing at the top. Heat or water-sensitive ingredients such as perfume, bleach, activator and enzyme are conventionally post-added to the tower particles in a subsequent mixing or blending operation.

The crutcher slurry is preferably made by sequentially adding the various components thereof in the manner which will result in the most miscible, readily pumpable and non-setting slurry for spray drying. The order of addition of the various components may be varied, depending on the circumstances. Normally it is preferable for all or almost all of the water to be added to the crutcher first, preferably at about the processing temperature, after which the processing aids, such as density modifying agents, e.g. sodium polyacrylate and sodium toluene sulfonate, and other minor components, including pigments and fluorescent brighteners are added, followed by a supplementary builder, if present, such as sodium bicarbonate or carbonate and the bead strengthening agent, e.g. sodium citrate. Finally, the zeolite and any filler salts, such as sodium sulfate, are added to the crutcher mix. Usually, during such additions, each component will be mixed in thoroughly before addition of the next component but methods of addition may be varied,

depending on the circumstances, so as to allow co-additions when such are feasible. Sometimes component additions may be in two or more parts to effect good mixing, e.g. during zeolite addition. Different components may sometimes be pre-mixed before addition to speed the mixing process. Normally, mixing speed and power will be increased as the materials are added. For example, low speeds may be used until after admixing in of the supplementary builder and the bead strengthening agent, after which the speed may be increased during and after addition of the zeolite to provide a homogeneous slurry mix.

The temperature of the aqueous medium in the crutcher will usually be about room temperature or elevated, normally being in the 20 to 70°C range, and preferably from about 25 to 40°C. Heating the crutcher medium may promote solution of the water soluble salts of the mix and thereby increase miscibility, but the heating operation, when effected in the crutcher, can slow production rates. Temperatures higher than 70°C are usually avoided because of the possibility of decomposition of one or more crutcher mix components, e.g., sodium bicarbonate.

Crutcher mixing times to obtain thoroughly mixed homogeneous slurries can vary widely, from as little as five minutes in small crutchers and for slurries of higher moisture contents, to as much as two hours, in some cases, although 30 minutes is a preferable upper limit.

The uniform crutcher slurry is thereafter transferred in the usual manner to a spray drying tower, which is located near the crutcher. The slurry is normally dropped from the bottom of the crutcher to a positive displacement pump, which forces it at high pressure through spray nozzles into the spray tower (countercurrent or concurrent), wherein the droplets of the slurry fall through a hot drying gas to form absorptive particles or beads.

After drying, the product is screened to desired size, e.g., 10 to 100 mesh, U.S. Sieve Series, and is ready for application of a nonionic and/or anionic detergent overspray in a mixing drum onto the tumbling particles, the particles or beads being either in warm or cooled (to room temperature) condition. The nonionic detergent will usually be at an elevated temperature to assure that it will be liquid; yet, upon cooling to room temperature, desirably it will be a solid, often resembling a waxy solid. This characteristic will not adversely affect the flowability of the final composition because the nonionic detergent normally penetrates to below the bead surface.

Zeolite A-type aluminosilicate builder, usually hydrated, with about 15 to 25% of water of hydration is used advantageously as the zeolite of the present invention. Hydrated zeolites X and Y may be useful too, as may be naturally occurring zeolites that can act as detergent builders. Of the various zeolite A products, zeolite 4A, a type of zeolite molecule wherein the pore size is about 4 Angstroms, is often preferred. This type of zeolite is well known in the art and methods for its manufacture are described in the art such as in U.S. Patent 3,114,603.

The zeolite builders are generally of the formula

$$(Na_2O)_x \cdot (Al_2O_3)_y \cdot (SiO_2)_z \cdot w\, H_2O$$

wherein x is 1, y is from 0.8 to 1.2, preferably about 1, z is from 1.5 to 3.5, preferably 2 to 3 or about 2, and w is from 0 to 9, preferably 2.5 to 6. The crystalline types of zeolite which may be employed herein include those described in "Zeolite Molecular Series" by Donald Breck, published in 1974 by John Wiley & Sons, typical commercially available zeolites being listed in Table 9.6 at pages 747-749 of the text, such Table being incorporated herein by reference.

The zeolite builder should be a univalent cation exchanging zeolite, i.e., it should be an aluminosilicate of a univalent cation such as sodium, potassium, lithium (when practicable) or other alkali metal, or ammonium. A zeolite having an alkali metal cation, especially sodium, is most preferred, as is indicated in the formula shown above. The zeolites employed may be characterized as having a high exchange capacity for calcium ion, which is normally from about 200 to 400 or more milligram equivalents of calcium carbonate hardness per gram of the aluminosilicate, preferably 250 to 350 mg. eq./g., on an anhydrous zeolite basis. The hydrated zeolites normally have a moisture or water of hydration content in the range of 5 to 30%, preferably about 15 to 25% and more preferably 17 to 22%, e.g., about 20%. The zeolites, as charged to a crutcher slurry from which beads or particles are spray-dried, should be in finely divided state, with the ultimate particle diameters being up to 20 microns, preferably 0.01 to 8 microns mean particle size, e.g., 3 to 7 microns, if crystalline, and 0.01 to 0.1 micron, e.g., 0.01 to 0.05 micron, if amorphous. Although the ultimate particle sizes are much lower, usually the zeolite particles are of sizes within the range of No. 100 to 400 sieve, preferably No. 140 to 325 sieve, as charged to the crutcher.

The weight percent of zeolite in the crutcher slurry is at least about 5% for purposes of the invention,

preferably from about 5 to 50%, and most preferably from about 10 to 40%, by weight, based on the solids content of the slurry.

A nonionic detergent is conveniently added to the tower beads to form a detergent composition by post-spraying onto surfaces of the particles in a blender or mixing drum. Although various nonionic detergents of satisfactory physical characteristics may be utilized, including condensation products of ethylene oxide and propylene oxide with each other and with hydroxy-containing bases, such as nonyl phenol and Oxo-type alcohols, it is highly preferred that the nonionic detergent be a condensation product of ethylene oxide and higher fatty alcohol. In such products the higher fatty alcohol will normally be linear and of 10 to 20 carbon atoms, preferably 12 to 18 carbon atoms, and sometimes most preferably of 12 to 15 or 12 to 14 carbon atoms. Because such fatty alcohols are normally available commercially only as mixtures, the number of carbon atoms given are necessarily averages.

The ethylene oxide (EtO) contents of the nonionic detergents will normally be in the range of 1 to 15 moles of EtO per mole of higher fatty alcohol, although as much as 20 moles of EtO may be present. Preferably such EtO content will be 3 to 10 moles and more preferably it will be 6 to 7 moles, e.g., 6.5 or 7 moles per mole of higher fatty alcohol (and per mole of nonionic detergent). As with the higher fatty alcohol, the polyethoxylate limits given are also limits on the averages of the numbers of EtO groups present in the condensation product. Both broad ranges ethoxylates and narrow range ethoxylate (BRE's and NRE's) may be employed, with the difference between them being in the "spread" of number of ethoxylate groups present, which average within the ranges given. For example, NRE's which average 5 to 10 EtO groups per mole in the nonionic detergent will have at least 70% of the EtO content in polyethoxy groups of 4 to 12 moles of EtO and will preferably have over 85% of the EtO content in such range. BRE nonionic detergents have a broader range of ethoxy contents than NRE's, often with a spread from 1 to 15 moles of EtO when the EtO chain is in the 5 to 10 EtO range (average). Examples of the BRE nonionic detergents include those sold by Shell Chemical Company under the trademark Neodol®, including Neodol 25-7, Neodol 23-6.5 and Neodol 25-3. Supplies of NRE nonionic detergents have been obtained from Shell Development Company, which identifies such materials as 23-7P and 23-7Z, and from Hoechst, which identifies such preferred products as Tergitol® having one of the following designations: 24-L-60N, 24-L-45N, 24-L-75N and 26-L-60N.

Other useful nonionic detergent compounds include the alkylpolyglycoside and alkylpolysaccharide surfactants, which are well known in the art.

Among the anionic surface active agents useful in the present invention are those surface active compounds which contain an organic hydrophobic group containing from about 8 to 26 carbon atoms and preferably from about 10 to 18 carbon atoms in their molecular structure and at least one water-solubilizing group selected from the group of sulfonate, sulfate, carboxylate, phosphorate and phosphate so as to form a water-soluble detergent.

Examples of suitable anionic detergents include soaps, such as, the water-soluble salts (e.g., the sodium potassium, ammonium and alkanol-ammonium salts) of higher fatty acids or resin salts containing from about 8 to 20 carbon atoms and preferably 10 to 18 carbon atoms. Particularly useful are the sodium and potassium salts of the fatty acid mixtures derived from coconut oil and tallow, for example, sodium coconut soap and potassium tallow soap.

The anionic class of detergents also includes the water-soluble sulfated and sulfonated detergents having an aliphatic, preferably an alkyl radical containing from about 8 to 26, and preferably from about 12 to 22 carbon atoms. Examples of the sulfonated anionic detergents are the higher alkyl aromatic sulfonates such as the higher alkyl benzene sulfonates containing from about 10 to 16 carbon atoms in the higher alkyl group in a straight or branched chain, such as, for example, the sodium, potassium and ammonium salts of higher alkyl benzene sulfonates, higher alkyl toluene sulfonates and higher alkyl phenol sulfonates.

Other suitable anionic detergents are the olefin sulfonates including long chain alkene sulfonates, long chain hydroxyalkane sulfonates or mixtures of alkene sulfonates and hydroxyalkane sulfonates and hydroxyalkane sulfonates. The olefin sulfonate detergents may be prepared in a conventional manner by the reaction of SO_3 with long chain olefins containing from about 8 to 25, and preferably from about 12 to 21 carbon atoms, such olefins having the formula $RCH=CHR_1$ wherein R is a higher alkyl group of from about 6 to 23 carbons and R_1 is an alkyl group containing from about 1 to 17 carbon atoms, or hydrogen to form a mixture of sultones and alkene sulfonic acids which is then treated to convert the sultones to sulfonates. Other examples of sulfate or sulfonate detergents are paraffin sulfonates containing from about 10 to 20 carbon atoms, and preferably from about 15 to 20 carbon atoms. The primary paraffin sulfonates are made by reacting long chain alpha olefins and bisulfites. Paraffin sulfonates having the sulfonate group distributed along the paraffin chain are shown in U.S. Nos. 2,503,280; 2,507,088; 3,260,741; 3,372,188 and German Patent No. 735,096.

Other suitable anionic detergents are sulfated ethoxylated higher fatty alcohols of the formula RO-$(C_2H_4O)_mSO_3M$, wherein R is a fatty alkyl of from 10 to 18 carbon atoms, m is from 2 to 6 (preferably having a value from about 1/5 to 1/2 the number of carbon atoms in R) and M is a solubilizing salt-forming cation, such as an alkali metal, ammonium, lower alkylamino or lower alkanolamino, or a higher alkyl benzene sulfonate wherein the higher alkyl is of 10 to 15 carbon atoms. The proportion of ethylene oxide in the polyethoxylated higher alkanol sulfate is preferably 2 to 5 moles of ethylene oxide groups per mole of anionic detergent, with three moles being most preferred, especially when the higher alkanol is of 11 to 15 carbon atoms. A preferred polyethoxylated alcohol sulfate detergent is marketed by Shell Chemical Company as Neodol 25-3S.

The most highly preferred water-soluble anionic detergent compounds are the ammonium and substituted ammonium (such as mono, di and triethanolamine), alkali metal (such as, sodium and potassium) and alkaline earth metal (such as, calcium and magnesium) salts of the higher alkyl benzene sulfonates, olefine sulfonates and higher alkyl sulfates. Among the above-listed anionics, the most preferred are the sodium linear alkyl benzene sulfonates (LABS), and especially those wherein the alkyl group is a straight chain alkyl radical of 12 or 13 carbon atoms.

Cationic surface active compounds may also be employed. They comprise surface active detergent compounds which contain an organic hydrophobic group which forms part of a cation when the compound is dissolved in water, and an anionic group. Typical cationic detergents are amine and quaternary ammonium compounds.

The quaternary ammonium compounds useful herein are known materials and are of the high-softening type. Included are the N,N-di-(higher) C_{14}-C_{24}, N,N-di(lower) C_1-C_4 alkyl quaternary ammonium salts with water solubilizing anions such as halide, e.g. chloride, bromide and iodide; sulfate, methosulfate and the like and the heterocyclic imides such as imidazolinium.

For convenience, the aliphatic quaternary ammonium salts may be structurally defined as follows:

$$\left[\begin{array}{ccccc} & & R_1 & & \\ & & \vdots & & \\ R & \cdots & N & \cdots & R_2 \\ & & \vdots & & \\ & & R_3 & & \end{array}\right]^{+} \quad X^{-}$$

wherein R and R_1 represent alkyl of 14 to 24 and preferably 14 to 22 carbon atoms; R_2 and R_3 represent lower alkyl of 1 to 4 and preferably 1 to 3 carbon atoms, X represents an anion capable of imparting water solubility or dispersibility including the aforementioned chloride, bromide, iodide, sulfate and methosulfate. Particularly preferred species of aliphatic quats include:

distearyl dimethylammonium chloride
di-hydrogenated tallow dimethyl ammonium chloride
di tallow dimethyl ammonium chloride
distearyl dimethyl ammonium methyl sulfate
di-hydrogenated tallow dimethyl ammonium methyl sulfate.

A builder supplementary to the zeolite and the defined bead strengthening agents may be added to the crutcher slurry, if desired. Any suitable water soluble or water insoluble builder, either inorganic or organic, may be used for this purpose providing that it is useful as a builder for the particular nonionic detergent or mixture of detergents that may be employed. Such builders are well known to those of skill in the detergent art and include: alkali metal phosphates, such as alkali metal polyphosphates including alkali metal tripolyphosphates with the caveat that such alkali metal phosphates are preferably used only in the restricted amounts herein stipulated for a low-P product; alkali metal carbonates; alkali metal bicarbonates; alkali metal polyacrylates, e.g. sodium polyacrylate; alkali metal borates, e.g., borax and alkali metal gluconates.

Other components may be present in the detergent compositions to improve the properties and in some cases, to act as diluents or fillers. Among the suitable fillers, the most preferred is sodium sulfate. Illustrative of suitable adjuvants are enzymes, which may be present to promote cleaning of hard to remove stains from laundry or hard surfaces. Among enzymes, the most useful in laundering operations are the proteolytic and amylolytic enzymes. Other useful adjuvants are foaming agents, such as lauric myristic

diethanolamide, when foam is desired, and anti-foams, when desired, such as dimethyl silicone fluids. Also useful are bleaches, such as sodium perborate, which may be accompanied by suitable activator(s) to promote bleaching actions in warm or cold water. Flow promoting agents, such as hydrated synthetic calcium silicate, which is sold under the trademark Microcel® C, may be employed in relatively small proportions. Other adjuvants that are usually present in detergent compositions include fluorescent brighteners, such as the stilbene brighteners; perfumes; and colorants, including dyes and water dispersible pigments.

Among other components which may be added to compositions according to the invention there may be mentioned the copolymers of polyethylene terephthalate and polyoxyethylene terephthalate (PET-POET copolymers), which are known to be effective as soil release promoters.

The PET-POET copolymers employed will usually be of molecular weights in the range of 15,000 to 50,000, preferably 19,000 to 43,000, e.g., about 30,000 or 40,000, according to molecular weight determinations performed on samples of materials of such types. Such molecular weights are weight average molecular weights. In the polymers utilized, the polyoxyethylene will usually be of a molecular weight in the range of about 1,000 to 10,000 and the molar ratio of polyethylene terephthalates to polyoxyethylene terephthalate units will be within the range of 2:1 to 6:1. The proportion of ethylene oxide to phthalic moiety in the polymer will normally be at least 10:1 and often will be 20:1 or more. Thus, it is seen that the polymer may be considered as being essentially a modified ethylene oxide polymer with the phthalic moiety being only a minor component thereof, whether calculated on a molar or weight basis. A preferred PET-POET copolymer is obtained from Alkaril Chemical Company as Alkaril SRP-2-F, which also contains 5% of polyacrylate stabilizer.

EXAMPLE 1

A spray-dried detergent powder in accordance with the invention having the ingredients shown below was prepared as follows, all percentages referring to the crutcher slurry are based on the solids content of the slurry in the absence of water.

COMPONENT	WEIGHT PERCENT
Nonionic surfactant (Neodol® 25-7 sold by Shell Chemical Company)	12.4
Zeolite	35.5
Water	9.0
Sodium Carbonate	23.0
Sodium Polyacrylate	3.0
Sodium Citrate	5.0
Sodium Sulfate	9.0
Sodium Toluene Sulfonate	0.1
Adjuvants (brightener, perfume, enzyme, etc.)	Balance

An aqueous crutcher slurry is prepared by adding to water at 38 °C, 3% sodium polyacrylate and 0.1% sodium toluene sulfonate while mixing with a turbine blade mixer at a low speed (10-50 rpm). After about 1 minute of agitation, there is added to the slurry a brightener, 23% sodium carbonate and 5% sodium citrate while mixing at a high speed (100 rpm) for 1-2 minutes. Zeolite at a weight percent of 35.5 is then added in 4 equal parts to the slurry to insure proper mixing, followed by 9% sodium sulfate. The mixer speed during the latter additions is at 200 rpm. All of the aforementioned percentages being based on the solids content of the slurry, in the absence of water.

The finished batch temperature of the crutcher is about 55 °C and the solids content is 62%. From the crutcher, the slurry is dropped into a large hold tank *prior* to being pumped to a spray tower for spray drying. Typical spray pressures for this product are 500 pounds per square inch. Inlet air temperatures are about 400-450 °C with outlet air temperatures about 95-105 °C. The tower particles exiting the spray tower are transported to a rotary mixing drum where the nonionic surfactant heated to about 50 °C is oversprayed onto the tumbling particles. Adjuvants such as perfume, or enzyme are also added, if desired, to the mixing drum.

The finished particulate detergent composition may be used as a laundry composition or as a dishwashing detergent composition for automatic dishwashing machines.

EXAMPLE 2

For comparative purposes, the compositions of four commercial spray-dried No-P, zeolite-containing laundry detergent products sold in the United States are shown in Table I below and designated A-D. The presence or absence of adjuvants such as perfume, brightener and enzymes is not noted in the Table. Composition E is a spray-dried composition prepared in accordance with the present invention.

TABLE I

WEIGHT PERCENT OF COMPONENTS

COMPONENT	A	B	C	D	E
SURFACTANTS:					
ANIONIC	18.5	18.5	18.5		
NONIONIC	0.5	0.5	2.0	20.0	12.3
BUILDERS:					
CARBONATE	21	19.0	9.0	35.8	23.0
BICARBONATE	----	----	----	12.7	----
ZEOLITE	31	33.0	32.0	21.8	36.0
CITRATE	3.5	----	3.0	---	5.0
SILICATE	4.0	3.0	0.2	----	---
SULFATE	10.0	11.5	26.0	----	8.8
NaPAA[1]	3.0	3.0	4.0	----	3.0
PERBORATE	----	----	0.3	----	----
PEG[2]	2.0	2.0	2.0	----	---
WATER	Bal.	Bal.	Bal.	Bal.	Bal.

[1] Sodium Polyacrylate
[2] Polyethylene Glycol

The detergent compositions of Table I were each tested for mechanical strength by an empirical "Frangibility Test" (described below) which determines the frangibility (or resistance to breakage) of granular materials. Each of the compositions was also tested to determine the amount of residue (or insolubles) deposited on fabrics laundered with such composition; the test method used to rate each detergent composition being referred to as the "Residue Test" described below.

FRANGIBILITY TEST

The test method consists of placing 100 grams of 0% through 100 mesh granular material on a 100 mesh U.S. Std. sieve screen, adding three rubber balls, and shaking for two 15 minute periods. The amount of material that passes through the 100 mesh screen is weighed after 30 minutes. This figure is defined as the 100 mesh frangibility number.

The apparatus used consists of the following:

(a) U.S. Std. 100 mesh sieve, 8 inch diameter, with 2 inches of space above the screen.
(b) Eight inch diameter lid and receiving pan for the sieve.
(c) Three pure gum rubber balls, 1-3/8 inch diameter, 25-29 grams purchased from Southwest Engineering Co. (SWECO), 4800 Santa Fe Avenue, Los Angeles 58, CA, part No. 00-113.
(d) Ro-Tap sieve shaker purchased from VWR Scientific Company.
(e) Mass balance with a precision of ± 0.1 grams.

A. Preparing a 0% through 100 Mesh Sample

1. Place about 120-150 grams of the material to be tested on the 100 mesh screen.
2. Assemble the screen, receiving pan and cover and shake on the Ro-Tap sieve for five minutes.
3. Collect the material from the screen. If less than 100 grams remain on the screen, repeat steps A1-A3.

B. Test Procedure

1. Place 100 grams of material obtained in procedure A on a 100 mesh screen.
2. Assemble the screen and receiving pan and add three rubber balls to the material on the screen.
3. Cover the sieve-pan assembly and shake on the Ro-Tap sieve for 15 and 30 minutes.
4. Weigh and record the amount of -100 mesh material obtained after shaking. This amount is the frangibility number.

Frangibility numbers below 10% indicate a granular material having excellent mechanical strength and integrity. Numbers from 10% to 20% are considered good to acceptable from the standpoint of being able to withstand prolonged storage and handling without excessive particle breakage, and numbers above 20% indicate increasingly poor mechanical strength and likely particle fragmentation during storage and handling.

RESIDUE TEST

The apparatus used in the test method was a General Electric top-loading washing machine. The fabrics laundered consisted of a 3 lb. load of the following darkly colored mens garments (e.g., black, navy blue, brown or dark green): 63/35% polyester/cotton permanent press dress shirt; 100% nylon knit sport shirt; 100% polyester doubleknit or gabardine pants; and denim pants.

A wash load as described above was laundered in the General Electric machine under cold wash water conditions (10 °C) at a water level of 17 gallons containing 200 ppm water hardness. The wash cycle was five minutes. The wet garments were line-dried indoors and then evaluated for residue by a three member panel which checked for the following: specks, particles (large specks), streaks, smudges and polka-dots (a smudge circle).

Each dry garment was inspected for residue, and a numerical rating assigned for each garment according to the description below. The scale runs from 0 = none to 4 = severe. For example, a shirt with no residue corresponds to a "0" rating.

DESCRIPTION OF RESIDUE CLASSES

VERBAL CLASS	NUMERICAL CLASS	DESCRIPTION
None	0 to 0.5	None to very few tiny or small specks or particles.
Light	0.6 to 1.5	Few specks or particles of detergent and no more than a few light smudges.
Moderate	1.6 to 2.5	Several smudges and/or streaks and/or several to many specks.
Heavy	2.6 to 3.5	Many small specks to large particles and/or several to many streaks and/or several to many heavy smudges.
Severe	3.6 or greater	80% or more of the garment covered with specks, particles, and/or streaks and/or smudges.

After all items are individually rated, the values are added together for all garments in the load and the sum is divided by the number of garments to arrive at the average "Residue rating".

In Table 2 there is presented the Frangibility number and Residue rating for detergent compositions A through E.

TABLE 2

COMPOSITION	FRANGIBILITY(%)	RESIDUE RATING
A	16.8	2.3
B	13.0	2.6
C	11.7	2.1
D	25	0.5
E	5	less than 0.5

As noted in Table 2, only composition E, in accordance with the invention, had superior mechanical strength as reflected in a Frangibility number below 10, and virtually no residue deposited on laundered fabrics.

EXAMPLE 3

A detergent composition containing sodium citrate, surfactant and zeolite in the absence of sodium silicate similar to that described in EP 1853 published May 1979 at page 26 thereof (Example 4) is prepared by the process described in such Example for purposes of comparing its measured Frangibility relative to Composition E of the present invention described in Example 2. The comparative composition is designated "F" and described in Table 3 below.

TABLE 3

COMPONENT	*WEIGHT PERCENT OF COMPONENTS*
	E
SURFACTANTS:	
Anionic	*10.5*
Nonionic	*3.0*
BUILDERS:	
Sodium Tripolyphosphate	*4.0*
Bicarbonate	*12.0*
Zeolite	*20.0*
Sodium Citrate	*4.0*
Water	*Bal.*

In Table 4 there is presented the Frangibility number for Compositions E and F.

TABLE 4

COMPOSITION	FRANGIBILITY(%)
E	5
F	above 30

The measured strength and integrity of the particles of Composition E are far superior to that of Composition F, as reflected by the latter's high Frangibility number. This is attributed to the inclusion of substantial amounts of surfactant in the crutcher slurry in the preparation of Composition F in accordance with the practice of the prior art.

Claims

1. A process for producing a free-flowing spray-dried particulate detergent composition having a density of from about 0.3 to about 1.0 g/cc and containing a zeolite and at least one anionic, nonionic or cationic surface active detergent compound, said detergent composition having improved particle

mechanical strength and integrity to allow extensive storage and handling of the composition with only minimum breakage and abrasion of the particles concomitant with high solubility characteristics such that the amount of visible residue deposited on fabrics laundered with such detergent composition is significantly minimized comprising the steps of:

(a) forming an aqueous crutcher slurry containing (i) at least about 5%, by weight, of a zeolite; (ii) an effective amount of a bead strengthening agent selected from the group consisting of citric acid, water-soluble salts of citric acid, nitrilotriacetate, water-soluble salts of nitrilotriacetate and mixtures thereof; and (iii) from about 0 to 50%, by weight, of a supplementary detergent builder other than (i) and (ii); said crutcher slurry being substantially free of sodium silicate and bentonite and containing less than about 3%, by weight, of anionic and/or nonionic surface active detergent compounds, all percentages being based on the solids content of the slurry, in the absence of water;

(b) spray-drying the crutcher slurry of step (a) to produce spray-dried particles; and

(c) applying one or more anionic, nonionic and cationic surface active detergent compounds to the spray-dried particles in an amount sufficient to obtain the desired detergency or softening properties for said particulate detergent composition.

2. A process as in claim 1 wherein the crutcher slurry contains from about 10 to 40%, by weight, of zeolite.

3. A process as in claim 1 wherein the crutcher slurry is substantially free of anionic and nonionic detergent compounds.

4. A process as in claim 1 wherein said bead strengthening agent is present in an amount of at least about 3%, by weight.

5. A process as in claim 1 wherein in step (c) a nonionic detergent compound is oversprayed onto the spray-dried particles.

6. A process as in claim 1 wherein the bead strengthening agent is sodium citrate or magnesium citrate.

7. A process as in claim 1 wherein said crutcher slurry further contains a density modifying agent.

8. A process in accordance with claim 7 wherein said density modifying agent is sodium polyacrylate.

9. A process in accordance with claim 8 wherein the molecular weight of the polyacrylate is from about 40,000 to 60,000.

10. A process as in claim 1 wherein in step (c) the amount of anionic, nonionic and cationic detergent compounds applied to the spray-dried particles is from about 1 to 50%, by weight, of the finished detergent composition.

11. A spray-dried detergent composition produced by the process of claim 1.

12. A composition in accordance with claim 11 containing from about 10 to 40%, by weight, of zeolite.